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• **OHASHI, Masahiro**

5240032 (JP)

• **NISHIMURA, Yoshifumi**

5240044 (JP)

• **HASEGAWA, Takuya**

2330003 (JP)

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(74) Representative: **Harding, Charles Thomas**

D Young & Co

120 Holborn

London EC1N 2DY (GB)

(71) Applicant: **Asahi Kasei Chemicals Corporation**
Tokyo 100-8440 (JP)

(72) Inventors:

• **KONDO, Takahiko**

Yokohama-shi, Kanagawa 2320052 (JP)

(54) **MICROPOROUS POLYETHYLENE FILM**

(57) A microporous polyethylene film, including a blend that contains a high density polyethylene copolymer which has a melt index (MI) of 0.1 to 100 and a content of an α -olefin unit with 3 or more carbon atoms of 0.1 to 1% by mole; and a high density polyethylene which has a viscosity average molecular weight (Mv) of

at least 500000 to 5000000, wherein the above described blend has an Mv of 300000 to 4000000 and a content of an α -olefin unit with 3 or more carbon atoms of 0.01 to 1% by mole.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a microporous polyethylene film and a battery separator including the same.

BACKGROUND ART

[0002] Microporous polyethylene films are now used in various applications such as microfiltration films, battery separators, condenser separators and materials for fuel cells. When used as a battery separator, in particular, as a lithium ion battery separator, a microporous polyethylene film is required to not only have general physical properties such as mechanical strength and permeability, but also excel in "fuse effect" and "heat resistance" so as to secure the safety of the battery.

[0003] The mechanism of "fuse effect" in the film as a separator of a battery is such that when the inside of the battery is overheated due to over charge or the like, the separator fuses and forms a film that coats the electrodes to interrupt current flow, thereby ensuring the safety of the battery. It is known that in microporous polyethylene films, their fusing temperature, that is, the temperature at which their fuse effect develops is around 140°C; but on the other hand, from the viewpoint of stopping the runaway reaction in the inside of batteries as soon as possible, it is considered that the lower the fusing temperature, the better.

[0004] Furthermore, considering its function, the shape of the separator has to be maintained even after fusing so as to maintain the electrical insulation between the electrodes. This means that the separator, or microporous polyethylene film is required to excel in "heat resistance", as described above. The "heat resistance" can be considered from two aspects: film rupture properties and heat shrinkable properties. For example, to secure the safety of batteries at 150°C, US Standard, "Standard for Lithium Batteries" UL1642, stipulates a safety evaluation standard for batteries that require batteries to be stored in an oven at 150°C for 10 minutes. To come up to this safety standard, the separator is preferably such that after being made pore-free by fusing, it does not rupture at temperatures of 150°C or higher and undergoes the least possible heat shrinkage, thereby being able to maintain its shape. Any direct contact of the anode and cathode electrodes caused by film rupture or heat shrinkage, particularly heat shrinkage of wound battery body across its width induces a short circuit in the inside of the battery, whereby the battery becomes unsafe. Thus, there is a strong demand for a separator having excellent heat resistance.

[0005] It is important that film-rupture resistance and low heat shrinkability are compatible with each other, and only a separator having excellent film-rupture resistance and low heat shrinkability at the same time deserves being referred to as separator having excellent heat resistance.

[0006] A number of microporous films have been developed aiming at securing the safety of batteries, in other words, improving both the fuse effect and the heat resistance of batteries. However, in actuality, disclosed have been only technologies for microporous films excelling in either fuse effect or heat resistance, and thus it has been difficult to provide a microporous polyethylene film that satisfies both the general physical property requirements, such as mechanical strength and permeability, and the safety requirements, such as fuse effect and heat resistance.

[0007] For example, a technology for providing heat resistance to a microporous film and lowering the fusing temperature of the same has been known in which ultrahigh molecular weight polyethylene is blended with low molecular weight polyethylene or branched- or linear-low density polyethylene, as described in Patent Documents 1 and 2. This method is expected to provide a microporous film with heat resistance, owing to its ultrahigh molecular weight component, while lowering the fusing temperature of the film to some extent. However, blending ultrahigh molecular weight polyethylene simply with low molecular weight polyethylene is insufficient to lower the fusing temperature. Further, blending ultrahigh molecular weight polyethylene with branched- or linear-low density polyethylene so as to lower the fusing temperature more effectively makes film rupture likely to occur at the interface between the two types of polyethylene, because ultrahigh molecular polyethylene has a poor affinity for branched- or linear-low density polyethylene resulting in poor film-rupture resistance. Furthermore, increase in the amount of branched- or linear-low density polyethylene added lowers the degree of crystallinity of the film, thereby making it difficult to make the film porous, which poses a problem of affecting the permeability of the film.

[0008] There is proposed in Patent Document 3 a microporous polyethylene film produced by blending a specific high molecular weight polyethylene copolymer with high density polyethylene, thereby having a low fusing temperature and a certain degree of film rupture resistance. This microporous polyethylene film, however, still poses a problem of having increased heat shrinkage because it is composed of high molecular weight components alone.

[0009] There is proposed in Patent Document 4 a microporous polyethylene film which is composed of high density polyethylene and polyethylene having a specific melting point, thereby having a lower fusing temperature. However, it is difficult to allow a microporous polyethylene film to have mechanical strength, permeability and heat resistance in a well-balanced manner, while maintaining its low fusing temperature, by simply adding polyethylene having a specified

melting point, particularly when the film is made thin.

Patent Document 1: JP-A-2-21559

Patent Document 2: JP-A-5-25305

Patent Document 3: JP 3113287 (USP 6168858, EP 814117B1)

Patent Document 4: JP-A-2002-338730

DISCLOSURE OF THE INVENTION

[0010] Accordingly, the object of the present invention is to overcome the above described problems, thereby providing a microporous polyethylene having excellent mechanical strength and permeability, and besides, a low fusing temperature and high heat resistance.

[0011] After intensive examination of the amount of the copolymer contained in polyethylene, the molecular weight of polyethylene, etc., the present inventors have found that, surprisingly, a microporous polyethylene film which includes a blend containing polyethylene copolymer having a specific flowability and density is superior in balance of mechanical strength, permeability and heat resistance to conventional microporous polyethylene films that have a low fusing temperature.

[0012] Specifically, the present invention is as follows:

(1) A microporous polyethylene film, including a blend that contains a high density polyethylene copolymer which has a melt index (MI) of 0.1 to 100 and a content of an α -olefin unit with 3 or more carbon atoms of 0.1 to 1% by mole; and high density polyethylene which has a viscosity average molecular weight (Mv) of at least 500000 to 5000000, wherein the blend has an Mv of 300000 to 4000000 and a content of an α -olefin unit with 3 or more carbon atoms of 0.01 to 1% by mole.

(2) A microporous polyethylene film, including a blend that contains a high density polyethylene copolymer which has a melt index (MI) of 0.1 to 100 and a content of an α -olefin unit with 3 or more carbon atoms of 0.1 to 1% by mole; and homopolyethylene which has an Mv of at least 500000 to 5000000, wherein the blend has an Mv of 300000 to 4000000 and has a content of an α -olefin unit with 3 or more carbon atoms of 0.01 to 1% by mole.

(3) A microporous polyethylene film, including a blend that contains a high density polyethylene copolymer containing an α -olefin unit with 3 or more carbon atoms, and a high density polyethylene, characterized in that the microporous polyethylene film has a weight fraction measured by GPC of a component having a molecular weight of 1000000 or less is 1 to 40%, and a weight fraction measured by GPC of a component having a molecular weight of 10000 or less is 1 to 40%, the component having a molecular weight of 10000 or less has a content of an α -olefin unit with 3 or more carbon atoms of 0.1 to 1% by mole, and the blend has an Mv of 300000 to 4000000, and a content of an α -olefin unit with 3 or more carbon atoms of 0.1 to 1% by mole.

(4) The microporous polyethylene film according to any one of the above (1) to (3), wherein the above described α -olefin is propylene.

(5) The microporous polyethylene film according to any one of the above (1) to (4), wherein the above described polyethylene having an Mv of 500000 to 5000000 is a blend of two or three kinds selected from the following polyethylenes (A), (B) and (C):

(A) the above described polyethylene having an Mv of 1500000 or more and less than 5000000; (B) the above described polyethylene having an Mv of 600000 or more and less than 1500000; and (C) the above described polyethylene having an Mv of 250000 or more and less than 600000.

(6) The microporous polyethylene film according to any one of the above descriptions (1) to (4), wherein the above described polyethylene having an Mv of 500000 to 5000000 is an ultrahigh molecular weight polyethylene having an Mv of 1500000 or more.

(7) The microporous polyethylene film according to any one of the above descriptions (1) to (6), having a film rupture temperature of 150°C or higher.

(8) The microporous polyethylene film according to any one of the above descriptions (1) to (7), having a shrinkage force at 150°C of 2N or less.

(9) The microporous polyethylene film according to any one of the above (1) to (8), having a fusing temperature of 140°C or less.

(10) The microporous polyethylene film according to any one of the above (1) to (9), having a thickness of 5 to 24 μm .

(11) The microporous polyethylene film according to any one of the above (1) to (10), having a porosity of 30 to 70%.

(12) The microporous polyethylene film according to any one of the above (1) to (11), having an air permeability of 100 seconds or more and 600 seconds or less.

(13) A battery separator, including a microporous film according to any one of the above (1) to (12).

[0013] The microporous film of the present invention excels in mechanical strength, permeability and productivity and has a low fusing temperature and high heat resistance; and therefore, it is preferable as a battery separator.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014]

FIGS. 1A to 1C are views showing a measuring device for measuring the fusing temperature and short-circuit temperature of a film: FIG. 1A is a schematic view; FIG. 1B a plan view of nickel foil 2A; and FIG. 1C a plan view of nickel foil 2B.

BEST MODE FOR CARRYING OUT THE INVENTION

[0015] In the following the present invention will be described in detail in terms of its preferred embodiments.

[0016] In one embodiment, the microporous film of the present invention includes a blend of a high density polyethylene copolymer; and high density- or homo-polyethylene (hereinafter sometimes referred to simply as "blend").

[0017] From the viewpoint of flowability and shrinkage force relaxation at the time of shutdown and moldability, the melt index (MI) of the high density polyethylene copolymer is 0.1 to 100 and preferably 0.5 to 10. The viscosity average molecular weight (Mv) of the same is 10000 to 250000.

[0018] The comonomer of the high density polyethylene copolymer is an α -olefin with 3 or more carbon atoms (hereinafter sometimes referred to simply as "comonomer"), and examples of such comonomers include propylene, butane, pentene, hexane, heptene and octane. From the viewpoint of the affinity for other types of polyethylene, propylene, which has 3 carbon atoms, is most preferable of the above comonomers.

[0019] The amount of the α -olefin unit with 3 or more carbon atoms in the high density polyethylene copolymer is 0.1 to 1% by mole and preferably 0.2 to 0.8% by mole per 100% of ethylene unit in the same. If the amount is less than 0.1% by mole, the effect of lowering the melting point is not produced, whereas if the amount is more than 1% by mole, the degree of crystallinity of the resultant film lowers, resulting in a microporous film of poor permeability.

[0020] The density of the high density polyethylene copolymer needs to be high from the viewpoint of melting point and permeability, though it is related to the amount of the α -olefin unit with 3 or more carbon atoms contained in the polyethylene. The term "high density" herein used means 0.93 to 0.97 and preferably 0.94 to 0.96.

[0021] The high density polyethylene copolymer used in the present invention can be produced by various known processes. For example, it can be produced by polymerization using catalyst supported by a chromium compound, Ziegler catalyst containing magnesium compound or metallocene catalyst as disclosed in JP-B-1-12777.

[0022] The polyethylene blended with the high density polyethylene copolymer (hereinafter sometimes referred to simply as "polyethylene blended") is preferably high density polyethylene which contains less than 0.1% of comonomer unit or homopolyethylene which contains no comonomer. The term "high density" herein used may be defined as the same as that used in the above described a high density polyethylene copolymer.

[0023] Specifically, the microporous film of the present invention contains, besides the high density polyethylene copolymer, at least any one type of polyethylene selected from the above described types of polyethylene which has an Mv of 500000 to 5000000 and preferably 600000 to 4000000, and it may contain any several types of polyethylene selected from the above described types of polyethylene. The percentage of these types of polyethylene in the blend is preferably 10 to 90%, more preferably 30 to 85% and much more preferably 40 to 80%. Blending two or three types of polyethylene selected from the following types of polyethylene:

(A) polyethylene having an Mv of 1500000 or more and less than 5000000,

(B) polyethylene having an Mv of 600000 or more and less than 1500000, and

(C) polyethylene having an Mv of 250000 or more and less than 600000 is particularly preferable, because doing so increases the affinity among the types of polyethylene blended, thereby making it possible to fully draw out the heat resistance, which a high molecular weight component brings about, and fusing properties, which a high density polyethylene copolymer brings about.

[0024] The percentage of the high density polyethylene copolymer in the blend is, from the viewpoint of fusing properties and permeability, preferably 10 to 90%, more preferably 15 to 70% and much more preferably 20 to 60%. If the percentage is lower than 10%, the fusing properties become insufficient, whereas if the percentage is higher than 90%, the heating resistance becomes insufficient.

[0025] To further draw out the good fusing properties, which are brought about by the high density polyethylene

copolymer, it is preferable that the polyethylene blended is ultrahigh molecular weight polyethylene having an Mv of 1500000 or more.

[0026] In this case, the percentage of the high density polyethylene copolymer in the blend is, from the viewpoint of fusing properties and mechanical strength, preferably 10 to 90%, more preferably 30 to 85% and much more preferably 40 to 80%.

[0027] The Mv of the blend is, from the viewpoint of mechanical properties, preferably 300000 to 4000000, more preferably 400000 to 3000000 and much more preferably 500000 to 1000000. If the Mv is less than 300000, the heat resistance becomes insufficient, whereas if the Mv is more than 4000000, the viscosity becomes too high, and thus, the moldability becomes poor. The Mv of the blend in the present invention means the Mv of the blend of raw materials and/or that of the end product.

[0028] The amount of the comonomer unit contained in the blend is 0.01 to 1% by mole and preferably 0.1 to 0.8% by mole per 100% of ethylene unit.

[0029] Another embodiment of the present invention is a microporous polyethylene film, including a blend that contains a high density polyethylene copolymer containing α -olefin unit with 3 or more carbon atoms; and at least high density polyethylene having an Mv of 500000 to 5000000, characterized in that the weight fraction measured by GPC, of polyethylene having a molecular weight of 1000000 or less is 1 to 40%, that of polyethylene having a molecular weight of 10000 or less is 1 to 40%, the content of the α -olefin unit with 3 or more carbon atoms in the component having a molecular weight of 10000 or less is 0.1 to 1% by mole, the Mv of the blend is 300000 to 4000000 and the content of α -olefin unit with 3 or more carbon atoms is 0.01 to 1% by mole. In such a microporous polyethylene film, the component having a molecular weight of 1000000 or more and the component having a molecular weight of 10000 or less each preferably account for 1 to 40%, more preferably 1 to 30%, and much more preferably 1 to 20%, based on the molecular weight distribution measurement by GPC. If the percentage of each component falls in this range, the balance of the fusing properties, heat resistance and mechanical strength is further enhanced, which makes stretchability of the microporous polyethylene film better. To allow the blend to contain components having such molecular weights, the blend has to contain a high density polyethylene copolymer having an MI of 0.1 to 100 and at least polyethylene having an Mv of 500000 to 5000000.

[0030] The blend may contain polyethylene having an Mv higher than that of the high density polyethylene or any other polyolefin, as long as the performance of the blend is not impaired. Examples of such polyolefins include, not limited to, polypropylene, polymethylpentene and polybutene. Of these polyolefins, polyethylene is most preferable.

[0031] Then the preferable process for producing a microporous polyethylene film of the present invention will be described.

[0032] A microporous polyethylene film is produced by: first dissolving polyethylene in a solvent called plasticizer at temperatures higher than or equal to its melting point of the polyethylene, cooling the resultant solution to temperatures lower than or equal to its crystallization temperature to form polymer gel and using the polymer gel to form a film (film forming step); stretching the resultant film (stretching step); and removing the plasticizer (plasticizer removing step). In this production process, the order of the stretching step and the plasticizer removing step can be reversed.

[0033] The term "plasticizer" herein used means an organic compound compatible with polyethylene at temperatures lower than or equal to its boiling point. Concrete examples of such plasticizers include: decaline, xylene, dioctyl phthalate, dibutyl phthalate, stearyl alcohol, oleyl alcohol, decyl alcohol, nonyl alcohol, diphenyl ether, n-decane, n-dodecane and paraffin oil. Of these plasticizers, paraffin oil, dioctyl phthalate and decaline are particularly preferable.

[0034] The percentage of the plasticizer in the polymer gel is, not limited to, preferably 20% to 90% and more preferably 30% to 80%. If the percentage is less than 20%, a microporous film having a proper porosity is sometimes hard to obtain, whereas if the percentage is more than 90%, the viscosity of the heated solution is lowered, which sometimes makes hard the continuous molding of the polymer gel into a sheet.

[0035] In the following the process for producing a microporous polyethylene film will be described in terms of the above described three steps that constitute the process: film forming step; stretching step; and plasticizer removing step.

Film Forming Step

[0036] The process for forming a film is not limited to any specific one. A sheet having a thickness of several tens μm to several mm can be continuously formed by: for example, feeding mixed polyethylene powder and a plasticizer to an extruder; melt kneading both of the above materials at around 200°C; and casting the kneaded materials from an ordinary coat-hanger die to a cooling roll. The known inflation method may also be used. The method for feeding a raw material and a plasticizer in the above described process may be any known method in which resin and a plasticizer are fed in the completely solved state or in the slurry state. From the viewpoint of productivity, it is preferable to feed resin from a feed hopper and a plasticizer halfway to an extruder. In this case, the extruder may be provided with more than one feed opening for feeding a plasticizer.

[0037] In the above described process, powdered polyethylene having an average particle size of 1 to 150 μm is

preferably used because the use of such polyethylene makes the melt kneading operation more efficient. Particularly when using ultrahigh molecular weight polyethylene having a M_v as high as or higher than 1500000, the average particle size of the polyethylene is preferably 1 to 150 μm , more preferably 1 to 100 μm and particularly preferably 1 to 50 μm .
 5 [0038] Such powdery polyethylene, whose particle size is smaller than usual ones, may be prepared by sizing with a sieve or the like or can be produced by properly selecting a catalyst etc. in the step of polymerization.

Stretching Step

10 [0039] Then, the resultant sheet is stretched at least mono axially to form a stretched film. Examples of stretching methods applicable include: not limited to, tentering, rolling and rolling. Of these methods, simultaneous biaxial stretching by tentering is particularly preferably used. The stretching temperature is in the range of normal temperature to melting point of the polymer gel used, preferably 80 to 140°C and more preferably 100 to 130°C. The draw ratio, on an area basis, is preferably 4 to 400, more preferably 8 to 200 and much more preferably 16 to 100. If the draw ratio is less than 4, the strength of the film is not necessarily sufficient for a separator, whereas if the draw ratio is more than 400, the film
 15 can be sometimes hard to stretch and the porosity of the resultant microporous film can sometimes be low.

Plasticizer Removing Step

20 [0040] Then, the plasticizer is removed from the stretched film to obtain a microporous polyethylene film. The method for removing the plasticizer is not limited to any specific one. For example, when using paraffin oil or dioctyl phthalate as a plasticizer, it may be extracted with an organic solvent such as methylene chloride or methyl ethyl ketone. And if the resultant microporous film is dried under heat at temperatures lower than or equal to the fusing temperature, the removal of the plasticizer becomes better. For example, when using a low-boiling compound, such as decaline, as a plasticizer, the plasticizer can be removed only by drying the resultant microporous film under heat at temperatures
 25 lower than or equal to the fusing temperature of the microporous film. In either case, to prevent the physical properties of the resultant microporous film from deteriorating due to its shrinkage, it is preferable to remove the plasticizer while placing restrictions on the film, for example, keeping the film in the fixed state. The organic solvent used in the plasticizer removing step can be recycled after completing the plasticizer removing operation by a known method, such as distillation.
 30 [0041] To improve the permeability or the dimensional stability, it is also preferable to heat-treat the microporous polyethylene film produced by the above described process at temperatures as high as or lower than the fusing temperature of the film as necessary.

Physical Properties

35 [0042] The microporous polyethylene film obtained from the above described composition not only has mechanical strength and permeability equivalent to those of conventional microporous films, but also secure the high safety of batteries, when used as a battery separator.

40 [0043] The thickness of the microporous film of the present invention is preferably 1 to 500 μm , more preferably 5 to 100 μm and much more preferably 5 to 24 μm . If the thickness of the above described film is smaller than 1 μm , the mechanical strength may not always be sufficient, whereas if the thickness is larger than 500 μm , it may cause interference with the battery size and weight reduction.

[0044] The porosity of the microporous film of the present invention is preferably 30 to 70% and more preferably 35 to 50%. If the porosity is lower than 30%, the permeability may not always be sufficient, whereas if the porosity is higher than 70%, sufficient mechanical strength may sometimes not be obtained.

45 [0045] The air permeability is preferably 100 to 600 seconds, more preferably 120 to 550 seconds and much more preferably 150 to 500 seconds. If the air permeability is larger than 600 seconds, the permeability may not always be sufficient, whereas if the air permeability is smaller than 100 seconds, the pore diameter can sometimes be too large.

50 [0046] The puncture strength is, from the viewpoint of rupture resistance during the battery winding or inferior battery due to the short circuit between the electrodes, preferably 1 to 20 N/25 μm , more preferably 2 to 18 N/25 μm and particularly preferably 3 to 15 N/25 μm .

[0047] The fusing temperature is preferably 140°C or lower, more preferably 138°C or lower and much more preferably 135°C or lower so as to allow the microporous film to exert a current interrupting effect when the battery is heated due to over charge test or the like. If the fusing temperature is higher than 140°C, the current interruption by the shutdown may be delayed for example at an over charge test or the like, leading to the occurrence of exothermic reaction in the cell.

55 [0048] The film rupture temperature is preferably 150°C or higher and more preferably 155°C or higher. If the film rupture temperature is less than 150°C, the film as a separator may rupture at the time of battery test in an oven at 150°C.

[0049] The shrinkage force at 150°C is preferably 2N or smaller, more preferably 1.5N or smaller and much more preferably 1.0N or smaller. If the shrinkage force is larger than 2N, since the heat shrinkage force of the battery winding

material across the width is large at high temperature, the electrodes may come into contact with each other, thereby causing short-circuit inside the battery.

[0050] The shrinkage stress at 150°C is preferably less than 600 kPa, more preferably 300 kPa or smaller, much more preferably 200 kPa or smaller and still much more preferably 150 kPa or smaller.

[0051] The reason the microporous polyethylene film obtained from the above described composition can have both fusing properties and heat resistance at the same time, while maintaining mechanical strength and permeability equivalent to those of conventional microporous films, has not been clarified yet. However, the reason is probably that the high density polyethylene copolymer having a relatively low molecular weight has a low crystalline melting point, while maintaining its high density, and has an effect of lowering the fusing temperature without sacrificing its permeating performance, and besides, since the high density polyethylene copolymer has a high affinity for the high molecular weight component, film rupture, which occurs due to the interface between the components, does not occur during fusing, and the component having a low molecular weight contributes to making it relatively easier to relax the shrinkage force, which is a cause of heat shrinkage.

[0052] In the following, the present invention will be described in further detail by several examples. In the following examples and comparative examples, the term "parts" all means "parts by mass".

[0053] The testing methods used for testing the characteristics shown in examples and comparative examples are as follows.

(1) Film thickness

The film thickness was measured using a dial gauge (OZAKI MFG. CO., LTD.: "PEACOCK No. 25" (trademark)).

(2) Porosity

10 × 10 cm square samples were collected, and the volume and mass of the samples were measured. Then the porosity was calculated from the following equation using the measured values.

$$\text{Porosity (\%)} = (\text{Volume (cm}^3\text{)} - \text{Mass (g)}/\text{Density of polymer composition})/\text{Volume (cm}^3\text{)} \times 100$$

(3) Puncture strength

The puncture strength test was carried out using "KES-G5 Handy Compression Tester" (trademark), by KATO TECH CO. LTD. under the conditions: probe's tip curvature radius of 0.5 mm and puncture speed of 2 mm/sec. The maximum puncture load (N) was measured.

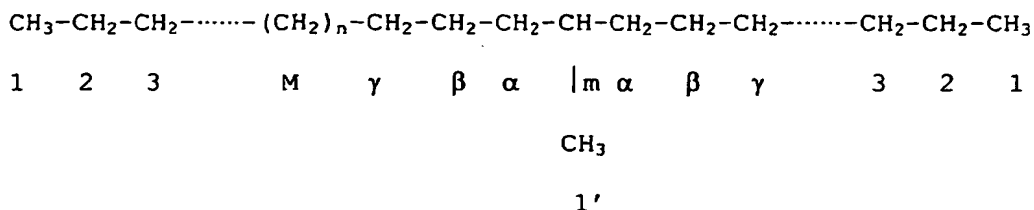
(4) Air permeability

The air permeability was measured with a Gurley air permeability tester in accordance with JIS P-8117.

(5) Content of comonomer units (Content of α -olefin unit with 3 or more carbon atoms)

The content of comonomer unit (% by mole) was obtained by: dividing the integral value (A), in molar terms, of signal intensity derived from comonomer by the sum of (A) and the integral value (B), in molar terms, of signal intensity derived from ethylene unit; and multiplying the obtained quotient by 100 in the ^{13}C -NMR spectrum.

When using propylene as a comonomer, for example, if the signal intensity of ^{13}C -NMR spectrum derived from the respective carbons in the following structural model are represented by I1, I1', I2, I3, I α , I β , I γ , I μ and I ν



the following equation holds:

$$\text{Content of comonomer unit (\% by mole)} = \frac{(A)}{[(A) + (B)]} \times 100$$

wherein (A) = $(l_1 + l_m + l_{\alpha}/2)/3$ and (B) = $(l_1 + l_2 + l_3 + l_m + l_{\alpha}/2 + l_{\beta} + l_{\gamma})/2$.

Since the effect of the terminals is small and therefore can be ignored, if the above described equation is arranged by considering l_1 , l_2 and l_3 as l_m and l_{α} , l_{β} and l_{γ} as $2l_m$, the following equation holds:

Content of comonomer unit (% by mole) =

$$I_m / [I_m + (I_M + 5I_m)/2] \times 100$$

(6) Melt index

The melt index measured at 190°C and a loading of 2.16 kg in accordance with JIS K-7210 was represented by MI.

(7) Fusing temperature/Film rupture (short-circuit) temperature

A schematic view of a measuring device for measuring the fusing temperature is shown in FIG. 1A. Reference numeral 1 denotes a microporous film, reference numerals 2A and 2B denote two sheets of nickel foil having a thickness of 10 μ m, and numerals 3A and 3B glass plates. Reference numeral 4 denotes an electric resistance meter (LCR meter "AG-4311" (trademark) manufactured by Ando Electric Co., Ltd.), which is connected to the two sheets of nickel foil 2A and 2B. Numeral 5 denotes a thermocouple, which is connected to a thermometer 6. Numeral 7 is a data collector, which is connected to the electric resistance meter 4 as well as the thermometer 6. Numeral 8 denotes an oven which is for heating the microporous film.

The measuring device will be described in further detail. As shown in FIG. 1B, the microporous film 1 is superimposed to the nickel foil 2A and fixed thereto lengthwise with "Teflon (trademark)" tape (the crosshatched portion of the figure). The microporous film 1 is impregnated with 1 mole/liter of lithium borofluoride solution (solvent: propylene carbonate/ethylene carbonate/ γ -butyl lactone = 1/1/2) as an electrolyte. As shown in FIG. 1C, "Teflon (trademark)" tape (the crosshatched portion of the figure) with a 15 mm \times 10 mm window portion at its center is laminated to the nickel foil 2B so that the nickel foil 2B is masked by the tape with the window portion left unmasked.

The two sheets of nickel foil 2A and nickel foil 2B are superimposed so that the microporous film 1 is sandwiched between them, and the two sheets of nickel foil having been superimposed are then sandwiched between the glass plates 3A and 3B. At this point, the window of the nickel foil 2B and the microporous film 1 are placed opposite to each other.

The two glass plates are fixed with a commercially available double clip. The thermocouple 5 is fixed to the glass plates with "Teflon (trademark)" tape.

The temperature and electric resistance of the microporous film 1 were continuously measured with the above described measuring device. The temperature was raised from 25°C to 200°C at a raising rate of 2°C/min and the electric resistance was measured with alternating current of 1 kHz. The term "fusing temperature" is defined as the temperature when the electric resistance of the microporous film reaches $10^3 \Omega$. Further, the term "film rupture (short-circuit) temperature" is defined as the temperature when the electric resistance of the microporous film becomes lower than $10^3 \Omega$ again after fusing.

(8) Shrinkage force and stress at the time of fusing

Measurements were made using TMA 50 (trademark) by Shimadzu Corporation. Samples cut to 3 mm width in the TD direction were fixed to chucks so that the distance between the chucks became 10 mm and then set on specialized probes. The initial loading was 0.0098 N (1.0 g) and the probe temperature was raised from 30°C to 200°C at a raising rate of 10°C/min, and the shrinkage force (N) generated was measured. Further, the shrinkage force (N) when the temperature reached 150°C was measured, and the measured value was used to calculate the shrinkage stress from the following equation:

Shrinkage stress (kPa) = [shrinkage force

$$(150^\circ\text{C}) / (3 \times T)] \times 100 \times 9.807 \times 10000$$

wherein T represents the thickness of a sample (μ m).

(9) Viscosity average molecular weight

Measurements were made in accordance with ASTM-D4020. The microporous film was dissolved in a decaline solution at 135°C, the intrinsic viscosity $[\eta]$ was measured, and the viscosity average molecular weight (Mv) was calculated from the following equation.

$$[\eta] = 6.77 \times 10^{-4} \text{ Mv}^{0.67}$$

(10) GPC

Measurements were made using 150C ALC/GPC (trademark) by Waters Corporation under the following conditions, and a calibration curve was prepared using standard polystyrene. A molecular weight distribution curve in polystyrene terms was obtained by multiplying each of the molecular weight components by 0.43 (Q factor of polyethylene/Q factor of polystyrene = 17.7/41.3). The molecular weight of the unfused matter was calculated by measuring the weight.

Column: two columns of GMH6-HT (trademark) +

two columns of GMH6-HTL (trademark) by TOSOH

CORPORATION

Mobile phase: o-dichlorobenzene
 Detector: differential refractometer
 Flow rate: 1.0 ml/min
 Column temperature: 140°C
 Sample concentration: 0.05 wt%

(11) Battery evaluation

Preparation of positive electrode

[0054] A slurry was prepared by dispersing in N-methylpyrrolidone (NMP) 92.2% by weight of lithium cobalt composite oxide LiCoO_2 as an active material, 2.3% by weight of flake graphite and of acetylene black as conductive materials, and 3.2% by weight of polyvinylidene fluoride (PVDF) as a binder. The slurry was coated on one side of aluminium foil 20 μm thick, which was to be a positive electrode current collector, with a die coater, dried at 130°C for 3 minutes, and compression molded with a roll pressing machine. The coating was performed so that the amount of the positive electrode active material coated was 250 g/m^2 and the bulk density of the active material was 3.00 g/cm^3 . The resultant positive electrode was cut to about 40 mm wide to take the form of a strip.

Preparation of negative electrode

[0055] A slurry was prepared by dispersing in purified water 96.9% by weight of synthetic graphite as an active material and 1.4% by weight of ammonium salt of carboxymethylcellulose and 1.7% by weight of styrene-butadiene copolymer latex as binders. The slurry was coated on one side of copper foil 12 μm thick, which was to be a negative electrode current collector, with a die coater, dried at 120°C for 3 minutes, and compression molded with a roll pressing machine. The coating was performed so that the amount of the negative electrode active material coated was 106 g/m^2 and the bulk density of the active material was 1.35 g/cm^3 . The resultant negative electrode was cut to about 40 mm wide to take the form of a strip.

Preparation of non-aqueous electrolyte

[0056] A non-aqueous electrolyte was prepared by dissolving LiPF_6 as a solute in a mixed solvent of ethylene carbonate/ethyl methyl carbonate = 1/2 (volume ratio) so that the concentration of LiPF_6 was 1.0 mole/liter.

Battery assembly

[0057] The above described microporous film separators, strip positive electrode and strip negative electrode were superimposed in the order of strip negative electrode, separator, strip positive electrode and separator and then wound more than one time into a swirl to prepare an electrode laminate. The electrode laminate was pressed into a flat sheet and packed in an aluminum container. The aluminum lead drawn out from the positive electrode current collector was

connected to the container wall, while the nickel lead drawn out from the negative electrode current collector being connected to the terminal on the container lid. Then, the above described non-aqueous electrolyte was poured into the container. The lithium ion battery thus produced was 6.3 mm thick, 30 mm wide and 48 mm high and designed to have a nominal service capacity of 620 mAh.

[0058] The battery was first charged at a current of 310 mAh (0.5 C) to a battery voltage of 4.2 V in the atmosphere at 25°C and continued to be charged for totaling 6 hours in such a manner as to throttle the current flow from 310 mAh while keeping the battery voltage at 4.2 V. To conduct an over charge test for this battery, the battery was charged at a current of 620 mAh (1.0 C) to a battery voltage (the maximum charged voltage) of 10 V. The degree of exothermic reaction occurring in this state was observed.

Example 1

[0059] First, 10.5 parts of a high density polyethylene copolymer having an MI of 0.8 (Mv of 150000) (comonomer: propylene, propylene unit content of 0.6% by mole, density of 0.95), 10.5 parts of high density homopolyethylene having an Mv of 300000 (MI of 0.05) (comonomer unit content of 0.0% by mole, density of 0.95), 5.2 parts of high density homopolyethylene having an Mv of 700000 (MI of less than 0.01) (comonomer unit content of 0.0% by mole, density of 0.95), 8.8 parts of ultrahigh molecular weight homopolyethylene having an Mv of 2000000 (comonomer unit content of 0.0% by mole, density of 0.94), and 0.3 parts of tetrakis-[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate]methane as an antioxidant were blended and fed to a twin screw extruder through a feeder. Then, 65 parts of liquid paraffin (P-350 (trademark) manufactured by Matsumura Oil Co., Ltd.) was poured into the extruder through a side feed, the blend was kneaded at 200°C, and the kneaded blend was extruded from a T die fixed to the tip of the extruder, followed by cool solidification with a cast roll having been cooled to 25°C to form a gel sheet 1200 µm thick. The gel sheet was stretched at 120°C to 7- × 7-fold size with a simultaneous biaxial stretching machine, and the stretched film was immersed in methyl ethyl ketone to extract and remove the liquid paraffin and dried to obtain a microporous film. The obtained microporous film was heat fixed at 125°C. The physical properties of the obtained film are shown in Table 1. The molecular weight components calculated from the measurements of the film by GPC were as follows: the component having a molecular weight of 1000000 or more was 7% and the component having a molecular weight of 10000 or less was 5%.

Example 2

[0060] A microporous film was produced in the same manner as in example 1, provided that the polyethylene materials used were 10.5 parts of a high density polyethylene copolymer having an MI of 0.8 (Mv of 150000) (comonomer: propylene, propylene unit content of 0.6% by mole, density of 0.95), 14 parts of high density homopolyethylene having an Mv of 300000 (MI of 0.05) (comonomer unit content of 0.0% by mole, density of 0.95) and 10.5 parts of ultrahigh molecular weight polyethylene having an Mv of 2000000 (MI of less than 0.01) (comonomer unit content of 0.0% by mole, density of 0.94) and the thickness of the gel sheet was 1400 µm.

[0061] The physical properties of the obtained microporous film are shown in Table 1.

Example 3

[0062] A microporous film was produced in the same manner as in example 1, provided that the polyethylene materials used were 7 parts of a high density polyethylene copolymer having an MI of 1.0 (Mv of 120000) (comonomer: propylene, propylene unit content of 0.8% by mole, density of 0.94), 17.5 parts of high density homopolyethylene having an Mv of 300000 (MI of 0.05) (comonomer unit content of 0.0% by mole, density of 0.95) and 10.5 parts of ultrahigh molecular weight homopolyethylene having an Mv of 2000000 (MI of less than 0.01) (comonomer unit content of 0.0% by mole, density of 0.94) and the thickness of the gel sheet was 1000 µm.

[0063] The physical properties of the obtained microporous film are shown in Table 1.

Example 4

[0064] A microporous film was produced in the same manner as in example 1, provided that the polyethylene materials used were 14 parts of a high density polyethylene copolymer having an MI of 0.8 (Mv of 150000) (comonomer: propylene, propylene unit content of 0.6% by mole, density of 0.95) and 21 parts of high density homopolyethylene having an Mv of 700000 (MI of less than 0.01) (comonomer unit content of 0.0% by mole, density of 0.95). The physical properties of the obtained microporous film are shown in Table 1.

Example 5

[0065] A microporous film was produced in the same manner as in example 1, provided that the polyethylene materials used were 10.5 parts of a high density polyethylene copolymer having an MI of 2.0 (Mv of 100000) (comonomer: propylene, propylene unit content of 0.4% by mole, density of 0.95), 14 parts of high density homopolyethylene having an Mv of 300000 (MI of 0.05) (comonomer unit content of 0.0% by mole, density of 0.95) and 10.5 parts of ultrahigh molecular weight polyethylene having an Mv of 2000000 (MI of less than 0.01) (comonomer unit content of 0.0% by mole, density of 0.94). The physical properties of the obtained microporous film are shown in Table 1.

Example 6

[0066] A microporous film was produced in the same manner as in example 1, provided that the polyethylene materials used were 26.3 parts of a high density polyethylene copolymer having an MI of 0.8 (Mv of 150000) (comonomer: propylene, propylene unit content of 0.6% by mole, density of 0.95) and 8.8 parts of ultrahigh molecular weight polyethylene having an Mv of 3000000 (MI of less than 0.01) (comonomer unit content of 0.0% by mole, density of 0.93, average particle size of 35 μm). The physical properties of the obtained microporous film are shown in Table 1. The molecular weight components calculated from the measurements of the film by GPC were as follows: the component having a molecular weight of 1000000 or more was 7% and the component having a molecular weight of 10000 or less was 7%.

Example 7

[0067] A microporous film was produced in the same manner as in example 1, provided that the polyethylene materials used were 29.8 parts of a high density polyethylene copolymer having an MI of 0.8 (Mv of 150000) (comonomer: propylene, propylene unit content of 0.6% by mole, density of 0.95) and 5.3 parts of ultrahigh molecular weight polyethylene having an Mv of 4500000 (MI of less than 0.01) (comonomer unit content of 0.0% by mole, density of 0.93, average particle size of 60 μm). The physical properties of the obtained microporous film are shown in Table 1.

Example 8

[0068] A microporous film was produced in the same manner as in example 1, provided that the stretching temperature was 117°C. The physical properties of the obtained microporous film are shown in Table 1.

Example 9

[0069] A microporous film was produced in the same manner as in example 1, provided that the thickness of the gel sheet was 900 μm and the stretching temperature was 115°C. The physical properties of the obtained microporous film are shown in Table 1.

Comparative Example 1

[0070] A microporous film was produced in the same manner as in example 1, provided that the polyethylene material used was 35 parts of high density homopolyethylene having an Mv of 700000 (MI of less than 0.01) (comonomer unit content of 0.0% by mole, density of 0.95). The physical properties of the obtained microporous film are shown in Table 1.

Comparative Example 2

[0071] A microporous film was produced in the same manner as in example 1, provided that the polyethylene material used was 35 parts of a high density polyethylene copolymer having an MI of 0.8 (Mv of 150000) (comonomer: propylene, propylene unit content of 0.6% by mole, density of 0.95). The physical properties of the obtained microporous film are shown in Table 1.

Comparative Example 3

[0072] A microporous film was produced in the same manner as in example 1, provided that the polyethylene materials used were 10.5 parts of copolymerized low density polyethylene having an MI of 0.3 (Mv of 170000) (comonomer: butene, butene unit content of 1.8% by mole, density of 0.92), 14 parts of high density homopolyethylene having a viscosity average molecular weight of 300000 (MI of 0.05) (comonomer unit content of 0.0% by mole, density of 0.95) and 10.5 parts of high density homopolyethylene having an Mv of 2000000 (MI of less than 0.01) (comonomer unit

content of 0.0% by mole, density of 0.95). The physical properties of the obtained microporous film are shown in Table 1.

Comparative Example 4

[0073] A microporous film was produced in the same manner as in example 1, provided that the polyethylene materials used were 10.5 parts of high density homopolyethylene having an Mv of 150000 (MI of 0.8) (comonomer unit content of 0.0% by mole, density of 0.97), 14 parts of high density homopolyethylene having an Mv of 300000 (MI of 0.05) (comonomer unit content of 0.0% by mole, density of 0.95) and 10.5 parts of ultrahigh molecular weight polyethylene having an Mv of 2000000 (MI of less than 0.01) (comonomer unit content of 0.0% by mole, density of 0.95). The physical properties of the obtained microporous film are shown in Table 1.

Comparative Example 5

[0074] A microporous film was produced in the same manner as in example 1, provided that 9 parts of polyethylene copolymer having an MI of 3.0 (Mv of 70000, melting point of 127°C, hexane unit content of 1.3% by mole, density of 0.94) and 36 parts of high density homopolyethylene having an Mv of 280000, and 55 parts of liquid paraffin were used. The physical properties of the obtained microporous film are shown in Table 1.

Comparative Example 6

[0075] A microporous film was produced in the same manner as in example 1, provided that 17.1 parts of copolymerized linear high density polyethylene having an MI of 0.8 (Mv of 120000) (comonomer: propylene, propylene unit content of 1.3% by mole, density of 0.94), 15.2 parts of high density homopolyethylene having an Mv of 600000 and 5.7 parts of high density homopolyethylene having an Mv of 100000, as polyethylene materials, and 62 parts of liquid paraffin were used. The physical properties of the obtained microporous film are shown in Table 1.

Table 1

Composition		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Copolymerized linear high density PE1	NI0.8, comonomer 0.6%	30	30	-	40	-	75	85	30	30
Copolymerized linear high density PE2	NI1.0, comonomer 0.8%	-	-	20	-	-	-	-	-	-
Copolymerized linear high density PE3	NI2.0, comonomer 0.4%	-	-	-	-	30	-	-	-	-
Copolymerized linear high density PE4	NI3.0, comonomer 1.3%	-	-	-	-	-	-	-	-	-
Copolymerized linear high density PE5	NI0.8, comonomer 1.3%	-	-	-	-	-	-	-	-	-
Copolymerized linear low density PE	NI0.3, comonomer 01.3%	-	-	-	-	-	-	-	-	-
High density PE1	100000	-	-	-	-	-	-	-	-	-
High density PE2	150000	-	-	-	-	-	-	-	-	-
High density PE3	300000	30	40	50	-	40	-	-	30	30
High density PE4	600000	-	-	-	-	-	-	-	-	-
High density PE5	700000	15	-	-	60	-	-	-	15	15
Ultrahigh molecular weight PE1	2000000	25	30	30	-	30	-	-	25	25
Ultrahigh molecular weight PE2	3000000	-	-	-	-	-	25	-	-	-
Ultrahigh molecular weight PE3	4500000	-	-	-	-	-	-	15	-	-

- to be cont'd -

Table 1 (Cont'd)

Composition		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
Copolymerized linear high density PE1	MI0.8, comonomer 0.6%	-	100	-	-	-	-
Copolymerized linear high density PE2	MI1.0, comonomer 0.8%	-	-	-	-	-	-
Copolymerized linear high density PE3	MI2.0, comonomer 0.4%	-	-	-	-	-	-
Copolymerized linear high density PE4	MI3.0, comonomer 1.3%	-	-	-	-	20	-
Copolymerized linear high density PE5	MI0.8, comonomer 1.3%	-	-	-	-	-	15
Copolymerized linear low density PE	MI0.3, comonomer 01.3%	-	-	30	-	-	-
High density PE1	100000	-	-	-	-	-	45
High density PE2	150000	-	-	-	30	-	-
High density PE3	300000	-	-	40	40	80	-
High density PE4	600000	-	-	-	-	-	40
High density PE5	700000	100	-	-	-	-	-
Ultrahigh molecular weight PE1	2000000	-	-	30	30	-	-
Ultrahigh molecular weight PE2	3000000	-	-	-	-	-	-
Ultrahigh molecular weight PE3	4500000	-	-	-	-	-	-

- to be cont'd -

Table 1 (cont'd)

Film Characteristics		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Film Mv	10000 unit	50	52	48	40	45	48	43	50	50
Film comonomer	mole %	0.2	0.2	0.5	0.3	0.1	0.5	0.6	0.2	0.2
Film thickness	µm	17	20	12	17	17	17	17	17	8
Porosity	%	40	42	38	40	40	42	43	40	40
Air permeability	sec	400	450	280	390	500	480	470	400	200
Puncture strength	N	5.1	6	4.5	5.4	5	4.7	4.6	6	4.5
Fusing temperature	°C	137	137	135	135	135	132	130	137	137
Film rupture temperature	°C	157	155	155	151	154	155	155	156	156
Shrinkage force (150°C)	N	0.50	0.60	0.35	0.46	0.45	0.46	0.45	0.92	1.9
Shrinkage stress (150°C)	kpa	99	100	98	90	89	90	88	180	800
Battery evaluation		no exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred

Table 1 (cont'd)

Film Characteristics		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
Film Mv	10000 unit	55	12	50	50	25	30
Film comonomer	mole %	0	0.6	0.6	0	0.7	0.2
Film thickness	μm	17	21	18	18	25	20
Porosity	%	40	45	36	41	40	41
Air permeability	sec	370	490	650	390	610	430
Puncture strength	N	5.1	3.4	4.1	4.5	5	4.9
Fusing temperature	$^{\circ}\text{C}$	141	132	134	139	130	131
Film rupture temperature	$^{\circ}\text{C}$	151	140	145	150	142	145
Shrinkage force (150 $^{\circ}\text{C}$)	N	1.0	Membrane ruptured	Membrane ruptured	Membrane ruptured	Membrane ruptured	Membrane ruptured
Shrinkage stress (150 $^{\circ}\text{C}$)	kPa	200	-	-	-	-	-
Battery evaluation		exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred	exothermic reaction occurred	no exothermic reaction occurred	no exothermic reaction occurred

INDUSTRIAL APPLICABILITY

[0076] The microporous film of the present invention can be suitably used in the fields of, for example, microfiltration films, battery separators, condenser separators and fuel cell materials.

Claims

1. A microporous polyethylene film, comprising a blend that comprises a high density polyethylene copolymer which

has a melt index (MI) of 0.1 to 100 and a content of an α -olefin unit with 3 or more carbon atoms of 0.1 to 1% by mole; and a high density polyethylene which has a viscosity average molecular weight (Mv) of at least 500000 to 5000000, wherein the blend has an Mv of 300000 to 4000000 and a content of an α -olefin unit with 3 or more carbon atoms of 0.01 to 1% by mole.

2. A microporous polyethylene film, comprising a blend that comprises a high density polyethylene copolymer which has a melt index (MI) of 0.1 to 100 and a content of an α -olefin unit with 3 or more carbon atoms of 0.1 to 1% by mole; and a homopolyethylene which has an Mv of at least 500000 to 5000000, wherein the blend has an Mv of 300000 to 4000000 and has a content of an α -olefin unit with 3 or more carbon atoms of 0.01 to 1% by mole.
3. A microporous polyethylene film, comprising a blend that comprises a high density polyethylene copolymer comprising an α -olefin unit with 3 or more carbon atoms, and a high density polyethylene which has an Mv of at least 500000 to 5000000, characterized in that the microporous polyethylene film has a weight fraction measured by GPC of a component having a molecular weight of 1000000 or less of 1 to 40%, and a weight fraction measured by GPC of a component having a molecular weight of 10000 or less of 1 to 40%, the component having a molecular weight of 10000 or less has a content of an α -olefin unit with 3 or more carbon atoms of 0.1 to 1% by mole, and the blend has an Mv of 300000 to 4000000, and a content of an α -olefin unit with 3 or more carbon atoms of 0.01 to 1% by mole.
4. The microporous polyethylene film according to any one of claims 1 to 3, wherein the α -olefin is propylene.
5. The microporous polyethylene film according to any one of claims 1 to 4, wherein the polyethylene having an Mv of 500000 to 5000000 is a blend of two or three kinds selected from the following polyethylenes (A), (B) and (C):
 - (A) the polyethylene having an Mv of 1500000 or more and less than 5000000; (B) the polyethylene having an Mv of 600000 or more and less than 1500000; and (C) the polyethylene having an Mv of 250000 or more and less than 600000.
6. The microporous polyethylene film according to any one of claims 1 to 4, wherein the polyethylene having an Mv of 500000 to 5000000 is an ultrahigh molecular weight polyethylene having an Mv of 1500000 or more.
7. The microporous polyethylene film according to any one of claims 1 to 6, having a film rupture temperature of 150°C or higher.
8. The microporous polyethylene film according to any one of claims 1 to 7, having a shrinkage force at 150°C of 2N or less.
9. The microporous polyethylene film according to any one of claims 1 to 8, having a fusing temperature of 140°C or lower.
10. The microporous polyethylene film according to any one of claims 1 to 9, having a thickness 5 to 24 μm .
11. The microporous polyethylene film according to any one of claims 1 to 10, having a porosity of 30 to 70%.
12. The microporous polyethylene film according to any one of claims 1 to 11, having an air permeability of 100 seconds or more and 600 seconds or less.
13. A battery separator, comprising a microporous film according to any one of claims 1 to 12.

FIG. 1A

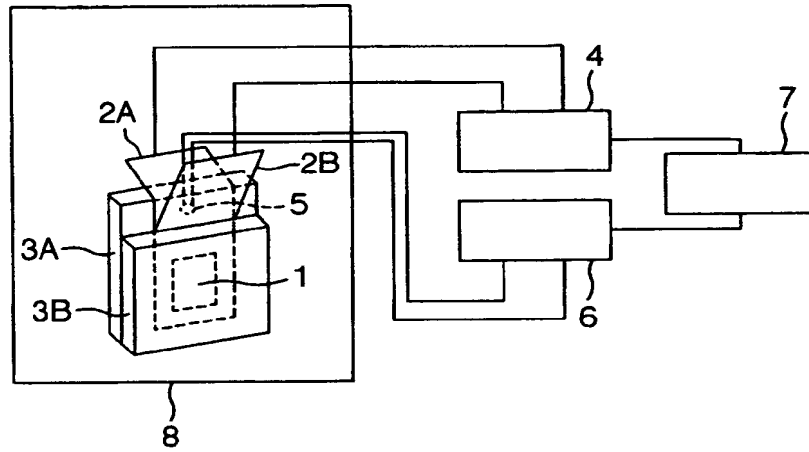


FIG. 1B

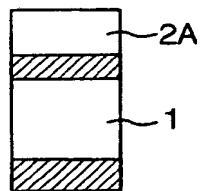
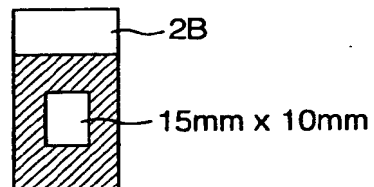


FIG. 1C



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/003901

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C08J9/00, 9/26, H01M2/16		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ C08J9/00, 9/26, H01M2/16		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Jitsuyo Shinan Toroku Koho 1996-2004 Kokai Jitsuyo Shinan Koho 1971-2004 Toroku Jitsuyo Shinan Koho 1994-2004		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97/20883 A1 (Asahi Chemical Industry Co., Ltd.), 12 June, 1997 (12.06.97), Full text & EP 877046 A1	1-13
A	JP 2000-1557 A (Kao Corp.), 07 January, 2000 (07.01.00), Full text (Family: none)	1-13
A	JP 10-292059 A (Mitsui Chemicals, Inc.), 04 November, 1998 (04.11.98), Full text (Family: none)	1-13
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 19 May, 2004 (19.05.04)		Date of mailing of the international search report 01 June, 2004 (01.06.04)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/003901

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	JP 2003-217554 A (Asahi Kasei Corp.), 31 July, 2003 (31.07.03), Full text (Family: none)	1-13

Form PCT/ISA/210 (continuation of second sheet) (January 2004)